Mechanically robust nacre-mimetic framework constructed polypyrrole-doped graphene/nanofiber nanocomposites with improved thermal electrical properties

Zhong Wang [a,b], Liuting Mo [a,b], Shujun Zhao [a,b], Jianzhang Li [a,b], Shifeng Zhang [a,b,*], Anmin Huang [c,*]

[a] MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China
[b] Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing 100083, China
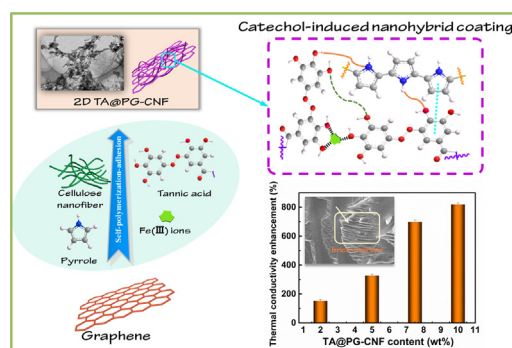[c] Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, China

HIGHLIGHTS

- We report on nacre-mimetic structure of graphene nanosheets/cellulose nanofiber film by generating polypyrrole nanohybrids.
- Natural tannic acid-induced the formation of the interconnected network acted as high efficient conductive networks.
- Significantly increased thermal and electrical conductivity were achieved at comparatively low filler content.
- Highly aligned network dominated the loading and heat transfer for strong and conductive graphene-based composites.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Nacre mimetics show great potential as mechanically robust, lightweight, and promising functional materials. Herein, we report a nanostructured nacre-mimetic hybrid framework, prepared via in situ self-polymerization of tannic acid (TA) and pyrrole monomer on cellulose nanofiber (CNF)-anchored graphene nanosheets (GNs), as a two-dimensional interconnected network (designated as TA@PG-CNF) to fabricate mechanically robust and thermally and electrically conductive composites. A unique network structure with a combination of conductive polypyrrole (PPy) protrusions and multiscale nanofibers/nanoplates was obtained, where the nanohybrid protrusions acted as bridges that link the adjacent GNs and nanofibers. As a result, a composite with low filler loading (10.0 wt%) exhibited advantages for the combination of all properties, i.e., enhanced electrical and thermal conductivity (6.52 S cm^{-1} and 7.81 W m^{-1} K^{-1}), high tensile strength (217.9 MPa), and good toughness (19.6 MJ m^{-3}). We attribute the enhancement of these properties to the construction of an interconnected TA@PG-CNF skeleton and the oriented "brick-and-mortar" structure based on GNs blocks and the polyvinyl alcohol matrix, in which a mechanically robust conductive network was constructed. We envision that the relevant functionalities can be integrated into stiff and strong bioinspired materials as flexible microelectronic candidates.

© 2018 Elsevier Ltd. All rights reserved.

* Corresponding authors at: MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China; Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, China.
E-mail addresses: shifeng.zhang@bjfu.edu.cn, (S. Zhang), ham2003@caf.ac.cn (A. Huang).

1. Introduction

The increasing evolution of miniaturization and high-degree integration of modern electronics have accelerated the development of advanced thermal-management materials with high strength and preferable electrical and thermal conductivities [1, 2]. Therein, graphene nanosheets (GNs) as a novel type of two-dimensional (2D) carbon material, are commendable candidates for highly conductive materials that not only possess ultrahigh thermal and electrical conductivities but also combine highly-flexible structure [3], enabling such materials to address energy storage and heat removal problems [4, 5]. However, these composites usually require high filler loadings [6], and the difficulty of regulation of their surface/interfacial structure restricts their comprehensive performance in terms of GNs applications [7].

As demonstrated previously, manipulating the interfacial interaction reduces the interfacial electrical/thermal resistance and thus improves the enhancement efficiency of the corresponding GNs composites [2, 8]. Particularly, the surface inertia of commercially available GNs [compared to easy functionalization of graphene oxide (GO)] leads to an insufficient combination effect with adjacent layers and/or the matrix [7, 9]. Therefore, various surface-functionalization approaches have been explored to tailor the interfacial structure and chemistry of the GNs, such as sonication-assistant exfoliation [10], solution-phase oxygen radical irradiation [11], and chemical/hybrid coating [12]. All of these studies mostly focused on addressing the influence of the GN/matrix interfaces. These enhancements of efficiency rely on the high GNs concentration in the composites by forming randomly dispersed filler-to-filler connections; however, they could give rise to the noticeably interfacial transfer resistance and suppress mechanical properties because of the formed filler-filler interfaces [4, 13]. Thus, more efficient improving strategies that allow regulation of GNs orientation and interfacial interactions at multilevel scales are of great significance to realize high thermal and electrical conductive composites with outstanding mechanical properties.

As a prime example, nacre-mimetic interface design is extensively concerned and has become one of the focuses in the construction of high-performance functional materials [14, 15]. Nacre mimetics are characterized by exhibiting a precise inorganic-organic interface, ordered brick-and-mortar structures with high level of reinforcements, and remarkable mechanical performance [16, 17]. Over the past decade, this "gold standard" has motivated scientists and engineers to prepare nacre-inspired composites based on different inorganic building blocks, such as clay [18], $CaCO_3$ [19], and graphene [20]. In terms of conducting graphene-based nacre-mimetics, most efforts have been focused on using reducing GO or GNs in combination with classical water-soluble polymers, such as poly(vinyl alcohol) (PVA) [21], polyelectrolytes [22], or polysaccharides [23]. However, the intrinsically electrically conductive polymers, especially the class of ionic polymers, have been hardly concerned in composite settings, which are of equal importance for their potential application as thermally and electrically conductive pathways in building blocks [18, 24]. Recent studies have demonstrated that using conducting polymers such as polypyrrole (PPy) [3], poly(3,4-ethylenedioxythiophene) polystyrene sulfonate [25], and poly(ionic liquid) [18], in combination with reducing GO or nanoclay would address this limitation and achieve improved conductive properties. For the case of interface design, electrically conductive polymers usually serve as conductivity bridges to connect the interfaces of inorganic bricks together [26], which is unavoidably restricted by the weak intermolecular interactions of polymers; thus, leading to poor mechanical cohesion and large interfacial contact resistance [7, 8]. Therefore, it is highly desirable to combine the superior interface design principle of nacre-mimetics with electrically conductive polymers to realize high strength and electrically conductive GN composites.

Mussel-inspired catecholamine chemistry offers a promising strategy to decorate versatile substrates through its extraordinary adhesion ability [27, 28], which should open a new way to construct multifunctional surfaces and particles [29]. Herein, based on the surface-independent adhesive mechanism of plant-derived tannic acid (TA, as shown in Fig. S1) and the secondary reaction between TA and PPy [30, 31], we report an in situ self-polymerization strategy to assemble hierarchical PPy-capped GNs nanohybrids in combination with abundant catechol moieties of TA on a cellulose nanofiber (CNF) framework. As building blocks, TA-functionalized nanohybrids (TA@PG-CNF) were directly introduced into PVA matrix to fabricate mechanically robust conductive composites (TA@PG-CNF/PVA) using a simple vacuum-assisted filtration method.

Our engineering strategy offers several distinct advantages, including: i) The CNF was used as a polymerizing template to overcome the difficulty of GNs dispersion, and its one-dimensional structure will be beneficial to form more oriented networks; ii) The TA@PG-CNF acting as 2D interconnected structures endowed the nacre-inspired composites with high thermal/electrical conductive networks induced by multiple interfacial interactions among multiscale components, leading to significant conductive reinforcement of the nanocomposites; iii) The employed ferric chloride ($FeCl_3$) acts as an oxidant to polymerize pyrrole into PPy leading to the simultaneous coordination cross-linking of catechol moieties on TA@PG-CNF nanohybrids. As a consequence, the as-prepared robust TA@PG-CNF/PVA displayed significantly enhanced thermal and electrical conductivities, a high anisotropy of thermal conductivity, as well as good mechanical properties, and could be useful in thermoelectric management applications.

2. Experimental

2.1. Materials

The GNs powder (average thickness, 3–5 nm and surface area, 40–60 m^{-2} g^{-1}) was purchased from Deyang Carbonene Co. Ltd. (Sichuan, China). The carboxyl-functionalized TEMPO-oxidized CNF aqueous dispersion (concentration, 0.4 wt%; 1.52 mmol g^{-1}) was obtained from Tianjin Haojia Cellulose Co., Ltd. (Tianjin, China). Pyrrole (98%) and ferric chloride ($FeCl_3$, 99.8%) were purchased from Beijing Chemical Reagents Co., Ltd. (Beijing, China). TA (95%), tri(hydroxymethyl) aminomethane (Tris, 99%), and PVA (PVA-1799) were purchased form Tianjin Heowns Biochem. Co., Ltd. (Tianjin, China). All regents were of analytical grade and used as received.

2.2. Preparation of the TA@PG-CNF nanohybrids

The TA@PG-CNF nanohybrids were prepared by incubating pristine GNs in the TA and CNF mixed aqueous solution with an optimized concentration at room temperature. In a typical procedure, GNs (0.2 g) were dispersed in the CNF dispersion (100 mL) with stirring and ultrasound into a 2 mg/mL suspension. Then, pyrrole (1.82 g) and TA (0.2 g) were added to the suspension (Tris-HCl, pH 8.5, 10 mM), maintained at 5 °C with continuous stirring, and $FeCl_3$ (3.12 g) was dissolved in 25 mL Tris-solution (pH 8.5, 10 mM) to form an oxidized solution. Later, the oxidized solution was dropped into the above mixture, followed by magnetic stirring for 6 h in an ice bath (5–8 °C). After the reaction, the TA@PG-CNF suspension was produced by centrifugation (15 min, 15,000 rpm) and several washes with deionized water. The concentration of the resulting hybrids was adjusted to 0.5 wt% using deionized water. In contrast, pure TA functionalized PPy/CNF (denoted as TA@PCNF) was also prepared by similar in situ polymerization of PPy in only CNF aqueous solution (without dispersing GNs), with the other conditions unchanged.

2.3. Fabrication of the TA@PG-CNF/PVA films

For the preparation of TA@PG-CNF/PVA composite films, the obtained TA@PG-CNF dispersions were mixed with 6.0 wt% PVA solution at different weight ratios. The mixture of TA@PG-CNF and PVA was